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Pressure effects in the triangular layered cobaltites Na_xCoO_2

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We have measured transport properties as a function of temperature and pressure up to 30 GPa in the Na_xCoO_2 system. For the $x=0.5$ sample, the transition temperature at 53 K increases with pressure, while paradoxically the sample passes from an insulating state to a metallic ground state. Compression on the $x=0.75$ sample transforms the sample from a metallic state to an insulating state. We discuss our results in terms of interactions between band structure effects and Na^+ order.

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The layered cobalt oxides of the type Na_xCoO_2 have been studied in recent years due to their unexpected high thermoelectric power[1] and the possibility of frustration of a one-half spin with antiferromagnetic interactions in a triangular lattice.[2] The interest increased when it was reported that by intercalating $Na_{0.3}CoO_2$ with water molecules, the material could be rendered superconducting[3] at $T_c^{SC} \sim 5$ K. On the other hand, the studies up to date have yielded a phase diagram in sodium concentration with properties essentially inverse to those envisioned.[4] Curie-Weiss behavior due to localized states is observed in concentrations near the band insulator point $(x=1)$, while more metallic delocalized dependences are measured near the Mott-Hubbard insulating concentration $(x=0)$. To the already complicated picture, the evidence of the presence of sodium ion ordering[5] at almost all concentrations[6] has added another crucial parameter to the problem. In spite of the large number of papers in the subject,[7–10] a full understanding of the electronic structure, or of the importance of charge ordering in transport properties and in superconductivity, has yet to be achieved.

We have performed a detailed pressure and temperature study of transport properties for two different Na concentrations, $x=0.75$ and $x=0.5$. For the compound $x=0.75$, we show that pressure causes an increase of the low temperature resistance. For the $x=0.5$ compound, we observe that the transition temperatures increase with pressure, while their effect on the transport properties disappears, down to a metallic state at the highest pressures.

The measured samples are powders from the same type of preparation as those of Ref. 4. $Na_{0.77}CoO_2$ was made by solid-state reaction of stoichiometric amounts of Na_2CO_3 and Co_3O_4 in oxygen at 800 °C. Sodium deintercalation was then carried out by treatment of samples in solutions obtained by dissolving I_2 $(0.2M, 0.04M)$ or Br_2 $(1.0M)$ in acetonitrile. After magnetic stirring for five days at ambient temperature, they were washed with copious amounts of acetonitrile, and multiple samples were tested by the inductively coupled plasma–atomic emission spectrometer method to determine the Na content.

The electrical resistance measurements were performed in a sintered diamond or carbon tungsten Bridgman anvil apparatus using a pyrophillite gasket and two steatite disks as the pressure medium.[11] The Cu-Be device that locked the anvils could be cycled between 4.2 and 300 K in a sealed Dewar. Three different pressure ranges: 0.7–8 GPa, 1.4–22 GPa, and 4–30 GPa were used on several powder samples of the $x=0.5$ and 0.75 compounds from the same batch. Due to the powder nature of our samples, no ambient pressure resistivity measurement was possible.

$Na_{0.5}CoO_2$. In Fig. 1, we show the variation of the electrical resistance–temperature dependence with pressure for the $x=0.5$ concentration. At the lowest pressures, we observe the transition to an insulating state as previously reported in monocrystal measurements.[4] Increasing compression diminishes the amplitude of the transition, which seems to disappear beyond ≈11 GPa, yielding to a metallic state at the highest pressures.

In fact, three anomalies have been previously reported. The first at 87 K, clearly detected by specific heat and magnetic susceptibility measurements,[12] but barely seen in the temperature derivative of the electrical resistivity of monocrystals. The second one at 53 K, associated with the devel-

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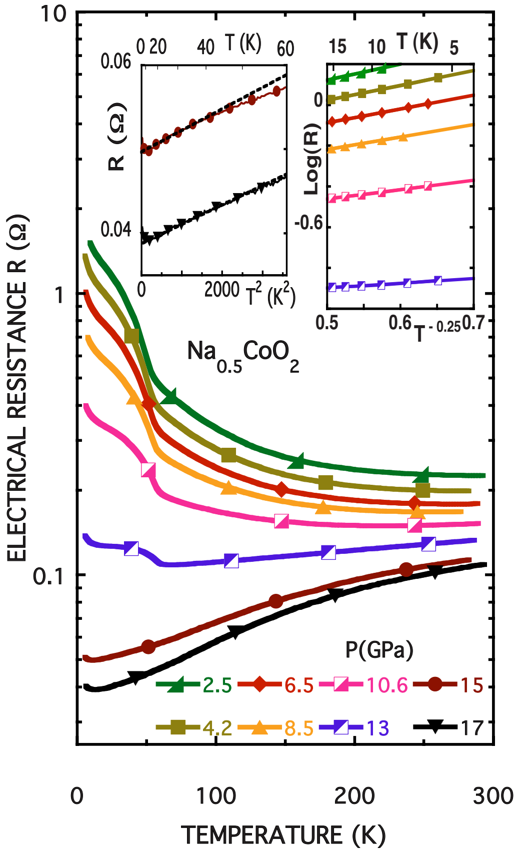

FIG. 1. (Color online) Temperature dependence of the electrical resistance of the $Na_{0.5}CoO_2$ sample D at different pressures. The transition toward an insulating ground state is clearly seen below 11 GPa. Above this pressure, the behavior is metallic. Left inset: Detail showing the T^2 at low temperatures for the highest pressures, where the samples are metallic (albeit a small residual localization at very low temperatures). Right inset: Plot showing the three-dimensional VRH behavior of the low temperature electrical resistance.

opment of the insulating state, which has been related to charge pinning on the subjacent Na cation order[4] or to a magnetic order.[13] The third one, more ill defined in temperature, at ~20 K has been linked to a second magnetic ordering in the Co spin network.[13] As for all metal-insulator transitions,[14] the logarithmic temperature derivative of the electrical resistance determines our transition temperatures. The powder nature of our sample does not allow us to detect the 87 K anomaly, but we observe the one at 53 K (T_c in Fig. 2) as a defined peak, as is expected for a second order phase transition.[14] We can follow with pressure the 20 K anomaly as a maximum of the logarithmic temperature derivative of the electrical resistance (T_* in Fig. 2). This anomaly does not have the form expected for a phase transition, but that corresponding to a crossover between two different transport regimes, e.g., from conducting to localized. In fact, it is shown on the inset of Fig. 1, where the logarithm of the electrical resistance for each pressure is plotted as a function of $T^{-1/4}$, the good agreement (linear behavior in the graph) of the data and the Mott variable-range-hopping[15] (VRH) law. Thus, it seems clear that the transition to an insulating state is, indeed, a crossover from a metallic behavior to a regime where defects localize the carriers remaining below T_c.

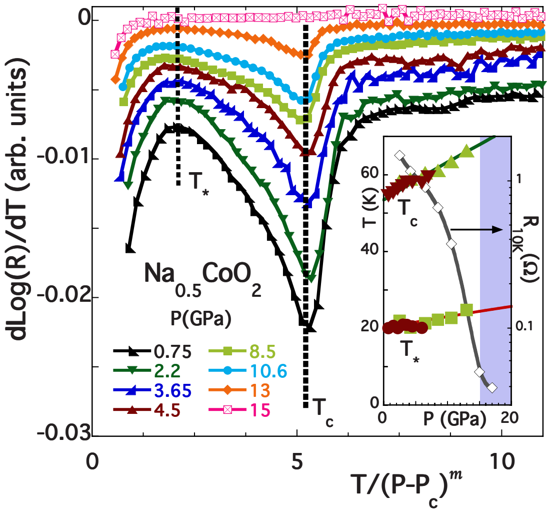

FIG. 2. (Color online) Logarithmic temperature derivative of the resistance of two $Na_{0.5}CoO_2$ samples (triangular symbols, sample C; other symbols, sample D) as function of temperature scaled by $|P-P_c|^m$, with $P_c=-28\pm 5$GPa and $m=0.6\pm 0.05$. Inset: Pressure dependence of the low temperature transition temperatures T_c (triangles) and T_* (dots and squares) for two $Na_{0.5}CoO_2$ samples (dark symbols, sample C; light symbols, sample D). The solid lines represent the scaling dependences $T^0_{ci}\cdot|P-P_c|^m$. We also show the 2 orders of magnitude fall of the 10 K resistance ($R_{10\text{ K}}$, white diamonds), which occurs while the transition temperatures increase with pressure. The region in pressure where the samples have a metallic behavior is shaded.

As shown in Fig. 2, we are able to perform a temperature scaling using the same standard quantum critical pressure dependence of the transition temperature for both anomalies, $|P-P_c|^m$, with $P_c=-28\pm 5$ GPa and $m=0.6\pm 0.05$. We find that the as-defined transition temperatures for both anomalies increase with pressure (inset of Fig. 2).

Paradoxically, while pressure seems to delocalize carriers, presumably gapped by the successive transitions, and renders the sample metallic, at the same time it increases the transition temperature and its correlated gap. This contrast is visible in the inset of Fig. 2, where, together with the transition temperatures, we have plotted the value of the resistance at 10 K as a function of pressure. We observe a decrease of the resistance of 2 orders of magnitude, leading to a metallic state, while the transition temperatures are augmented. As in an itinerant picture the transition temperature is directly related to the number of gapped carriers, an increase of the transition temperature should imply more gapped carriers and a more insulating ground state, not the more metallic ground state that we observe. A prompt and naïve explanation would be to assume that the magnetic and resistivity transitions are not related, though we discuss other interpretations below.

Interestingly, at the higher pressures, we obtain a resistivity with a Fermi liquid T^2 low temperature dependence (inset of Fig. 1) that can imply carrier-carrier or carrier-spin fluctuations scattering. However, some residual localization continues to exist at the lowest temperatures as shown by the

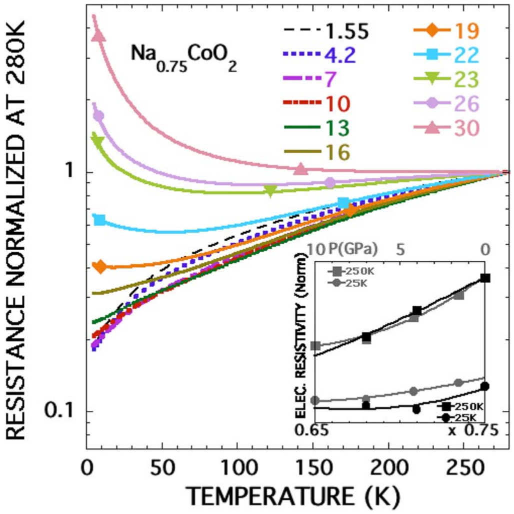

FIG. 3. (Color online) Temperature dependence of the electrical resistance of two $Na_{0.75}CoO_2$ samples normalized at 280 K (for clarity convenience) for different pressures. Inset: Comparison of the values of normalized resistivity for 250 and 25 K as a function of pressure (gray symbols, this work) and of sodium concentration (black symbols, from Ref. 4).

slight upturn tail. As similar T^2 resistivities have been observed in single crystal samples of the $x=0.31$ compound,[4] pressure apparently shifts the position of the sample toward the Na^+ depleted region of the phase diagram.

$Na_{0.75}CoO_2$. In Fig. 3, we show the resistance as a function of temperature for different pressures on an $x=0.75$ sample. At low pressures, we observe a trend toward a more metallic character, followed by a gradual upturn at low temperatures that at the highest pressure starts at ambient temperature. As in previous reports on powder samples,[16] we do not observe the transition at 20 K that signals magnetic ordering. Low pressure ($P \leqslant 1$ GPa) susceptibility measurements[17] on single crystals of this sodium concentration have shown a very strong increase of this transition with pressure ($dT_c/dP \approx 4$ K GPa^{-1}). Contrary to the $Na_{0.5}CoO_2$ case, we start here with a metallic state and end up with an almost insulating state at the highest pressure, implying a strong carrier localization with compression, for the highest pressures starting even at room temperature. We remark that a similar, but much less marked, behavior has been observed in the resistivity as a function of Na concentration.[4] In the inset of Fig. 3, we show the comparison of the two cases at two different temperatures, from where we estimate that the effect of 10 GPa would be equivalent to about 0.1 in Na concentration.

We begin the discussion by the apparent equivalency between pressure and Na concentration. Charge transfer under compression is a common concept in pressure measurements, as found in, e.g., cuprates[18] or manganites.[19] An instability toward slightly different valences of nonequivalent cobalt atoms has been suggested theoretically[9,20] and observed experimentally.[4,5] As discussed in Ref. 16, Na^+ ordering should contribute to this as a macroscopic occupation of the Na(1) site,[21] being directly above or below Co ions, presumably decreases their valence with respect to the other Co ions that just surround Na(2) sites. Pressure obviously increases this effect through a stronger compression of the c axis with respect to the a axis.[22] The extra charge localized by compression on the Co above (below) the Na(1) sites depletes the a_g band, as does a reduction of Na concentration. Thus, it seems reasonable to observe that the application of pressure is equivalent to a Na concentration decrease. This parallellism between pressure and Na concentration variation can also be expected from band structure calculations[10] that have shown that the oxygen z coordinate, half the thickness of the CoO_2 layer, is quadratically proportional to the Na concentration. As pressure compresses the z axis, we can expect, as a consequence, a change in the density of states at the Fermi level, which can be expressed as a change in Na concentration. We can estimate an order of magnitude value for this change, dx/dP. From Zhang *et al.*,[10] we obtain $dx/dz \approx 7$ Å^{-1} at $x=0.75$, and using the measured c parameter compressibility,[23] $\beta_c = 0.004$ GPa^{-1}, we find $dx/dP \approx 0.026$ GPa^{-1}, in agreement with the variation estimated from the inset of Fig. 3, $dx/dP \approx 0.01 \pm 0.008$ GPa^{-1}. This equivalence can explain both the increase of resistance at low temperatures in the $x=0.75$ compound and the metallization of the $x=0.5$ sample. We should stress, though, that this equivalence should be limited, as, e.g., steric effects due to the introduction of extra Na ions cannot be mimicked by pressure.

The insulating state observed at low temperatures in $Na_{0.5}CoO_2$ has been attributed either to a charge density wave (CDW) or to magnetic order or spin density wave (SDW), but it is, as we shall point out, more complex. The large majority of the CDW and/or SDW (DW) compounds (one, two, or even three dimensions; for a detailed list, see Ref. 24) that have been studied up to date yield a ratio gap Δ to transition temperature, $f = \Delta/(k_B T_{c1})$, much larger than the theoretical mean-field (MF) value, i.e., $f \approx 1.75$, going up to almost 10. Such large ratios have been attributed to phonon entropy,[25] to inelastic scattering of carriers by phonons,[24] or to deviations from perfect nesting in the SDW case.[26,27] The different and degenerate possibilities of nesting allow the formation of short range order (SRO) DW fluctuations at a temperature T_{MF} with the expected mean-field gap, but that have no long range order (LRO).[28]. The transition temperature observed in transport properties just signals the development of LRO at a temperature T_{LRO} much smaller than T_{MF}. The optical measurements[29,30] done on cobaltite samples compared to the transition temperature measured in transport properties yield $f \approx 1.75$, the mean-field value, which should be stressed as highly unusual. To obtain a mean-field value of f, external effects, such as commensurate pinning, are obligatory to stabilize the SRO fluctuations and allow the development of LRO near T_{MF}. We can, thus, speculate that the underlying Na^+ order may play an essential role in the appearance of the transition at T_{c1}, which corresponds to T_{LRO}, by stabilizing the DW [even under the assumption of a SDW, a small lattice distortion appears at T_{c1} (Ref. 31)] through matching pinning or Fermi surface reconstruction.[32] Compression will increase the interaction between the Na^+ order and the DW, probably leading to the increase of the transition temperatures that we observe with pressure.

In conclusion, we show that pressure enhances the low temperature transition temperatures in the $x=0.5$ compound, while the insulating ground state disappears under pressure. This result contradicts the present understanding of DW theory and its application to layered cobalt oxides. We speculate that the increase of the transition temperature is due to an enhancement of the ordered state due to stronger pinning by the Na^+ sublattice, and that the passage to a metallic ground state is due to depletion of the a_g band under pressure by electron pinning on Na(1) sites.

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